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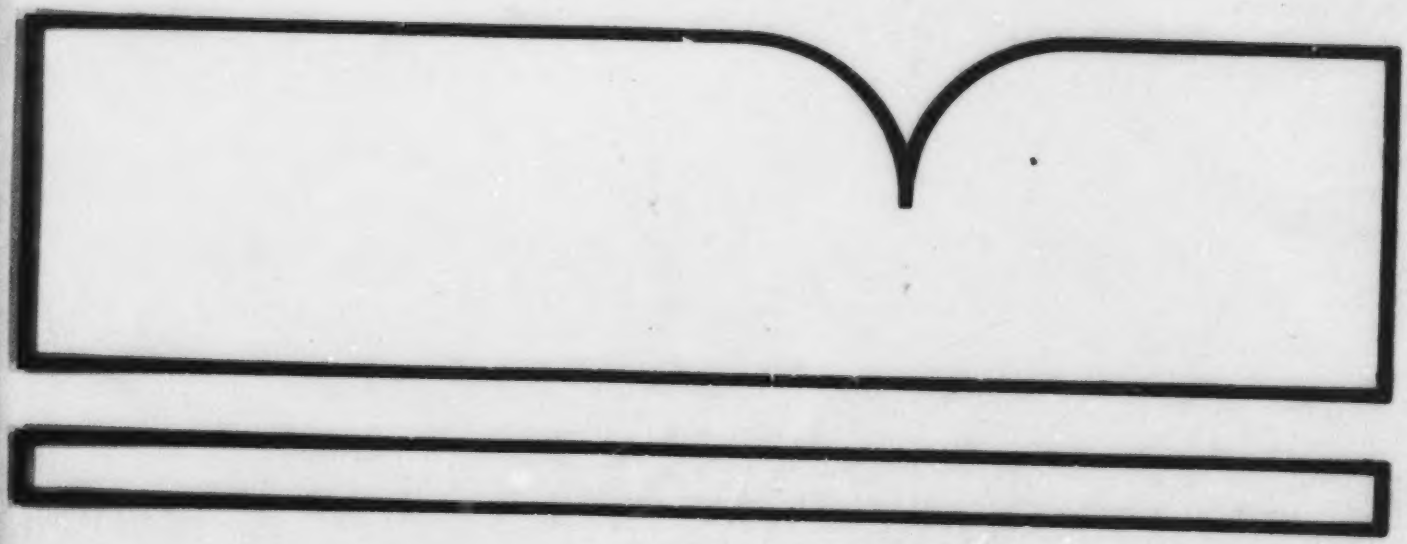

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Volume 4. Secondary Wastewater Treatment Plant Sludge from a Synthetic Manufacturing Plant

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report provides the results of a field study investigation of one of six sites receiving industrial waste sludges by land cultivation. The purpose of the study was to identify and verify parameters which lead to environmental acceptability of the waste, and to recommend research needs for establishing guidelines and criteria for land cultivation.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

This report presents the results of field measurements and observations of a land treatment site for the management of secondary wastewater treatment sludge from a synthetics manufacturing plant. The waste, composed of 8.5% solids, contained a large concentration of cellulose and nitrogen in a ratio amenable for soil improvement and plant growth. It also contained large quantities of sodium, which, unless properly managed, can adversely impact the soil structure. The site was sampled once, and observations were made on the type and amount of waste handled, site characteristics, and management procedures for waste application and monitoring. Organic and inorganic analyses were conducted on the waste and soil/waste mixture; inorganic analysis was performed on plant samples.

The site is a portion of land that is owned by the synthetics manufacturing plant. It is leased to farmers who cultivate wheat and corn. The geophysical characteristics (topography, meteorology, hydrology, etc.) of the site pose no significant concerns regarding possible contamination of the surrounding environment. However, soil texture deterioration is possible due to a combination of a soil with a high clay content and a waste with a large concentration of sodium. The waste generator is aware of this potential damage, which could lead to a decreased hydraulic conductivity of the soil. The site is managed to minimize salt build-up. Management methods include monitoring the soil and waste, and recording the frequency and location of waste applications.

The waste application site had wheat growing on it; at the time of observation these plants were taller and greener than the control site wheat plants. This may be due to the nitrogen and cellulose content in the waste which improves the soil texture and fertility.

The site had received waste for only a short period of time prior to sampling and for this reason, differences observed between control and application plots were not expected to be significant. The waste was incorporated into the soil according to normal agriculture practices, and the site is maintained to optimize plant yield and growth. Therefore, the waste/soil mixture was well aerated and irrigated which promotes rapid degradation of waste organic constituents. The inorganic and organic analysis of soil and plant samples indicated no significant differences between control and application sites. A possible, although statistically insignificant, trend toward accumulation of salt and aliphatic and aromatic hydrocarbons was observed in the top 0-6" of the soil.

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SECTION 1

INTRODUCTION

Land treatment is the application and incorporation of solid or semisolid waste into surficial soils. Other terms used to describe this practice include landfarming, land cultivation, refuse farming, land spreading, soil farming and soil incorporation. The term land application, on the other hand, usually refers to irrigation of surficial soil with wastewater. Land treatment is essentially a physical/chemical/biological waste treatment method that utilizes the natural capacity of the soil system to aerobically degrade, assimilate and immobilize certain waste constituents.

At every land treatment site, there is a dynamic balance of decomposition, attenuation and migration of waste constituents. The extent to which any of these mechanisms occurs depends on the waste character, site character and cultivation procedures.

A land treatment site should provide decomposition of the organic constituents applied and incorporated. The migration of soluble constituents from a land treatment site should be within environmentally acceptable concentrations for the receiving media, particularly ground and surface waters. The attenuation of remaining constituents over the design life of the site should not lead to a build up of total concentrations that could harm the soil structure, cause phytotoxicity, or lead to excessive concentrations in the food web through bioaccumulation.

From the above discussion, it is evident that specific site characteristics and waste characteristics together are key to achieving environmentally optimal use of surficial soils in waste treatment. Equally important (although not as evident) is the management of the land cultivation operation; no matter how optimal conditions may be for degradation/attenuation of waste, some sites can be overloaded. Management of a site can be viewed as the means through which desired waste treatment conditions are maintained.

OBJECTIVE

The objective of this project was to identify parameters which contribute to (or affect) the environmental acceptability of land treatment of a sludge from a synthetics manufacturing plant. The parameters are classified by waste characteristics (e.g., percent solids, salt content), site characteristics (e.g., topography, climate) and land treatment management procedures (e.g., soil aeration, frequency of waste application). Environmental acceptability was determined by comparing concentrations of waste constituents in the application area and control area suits, and by the potential for environmental contamination due to a combination of waste, assessing site and management parameters.

DESCRIPTION OF THE SITE

The identity of this site is protected by a confidentiality agreement included as part of the contract for this study. It is part of a 180-acre portion of land used for farming within the boundaries of an industrial complex where synthetics are manufactured. The waste generator owns the land and leases it to local farmers for wheat and corn production.

Waste Characteristics

The waste originates from an activated wastewater treatment system designed to treat effluent generated during manufacture of synthetics (SIC Code 3079). During treatment the waste is stripped of sulfides, neutralized and nitrogen and phosphate are added. The wastewater treatment sludge is centrifuged to 8.5% solids. Due to the difficulty of degrading cellulose-containing waste by other physical/chemical treatment methods, the waste generator turned to land treatment. Another advantage of land treatment was the high ratio of organic carbon to inorganic nitrogen in the waste; this characteristic offers soil-amending qualities to the clay soils of the region.

Site Characteristics

Prior to the construction of the synthetics plant (about 20 years ago) this 180 acre parcel was used for agriculture. Much of the land is leased to local farmers and continues to be under cultivation, mostly to wheat. Much of the adjacent area is also farmed, except for the area housing a second industrial facility located about a quarter of a mile to the west. To the best of facility personnel knowledge, the acreage presently being farmed will continue to be farmed during and following the use of the area for waste disposal.

Table 1 presents selected characteristics of the site. The terrain at the site presents minimal potential for site erosion. While overland erosion from cleared fields has occurred, it is attributed to the low permeabillity of the site, rather than land treatment activity.

Surface runoff from the site could discharge into the small tributary located near the site, although dense riparian vegetation along the stream bank traps most of the runoff before it enters the stream. The bank of the tributuary represents an important edge habitat and food source for faunal species. Elevated concentrations of toxic components in the food of the fauna could disrupt the ecology of this habitat. Fauna observed at this stream border are various species of migratory waterfowl, "food chain" game species (deer, doves, quail, pheasant) and game fish (catfish, carp and suckers) in the river.

The water table at the site is reportedly 30 to 60 meters below grade; the possibility of direct contact of waste materials with elevated groundwater tables is very low. Possibly, highly mobile salts could migrate to the groundwater over the long term.

TABLE 1. SELECTED PHYSICAL/CHEMICAL CHARACTERISTICS OF THE SITE

		Published Source*	Data from Site Visit/ Analysis**
I.	Soil Conditions		
	A. Soil Classification	Silty clay loam; moderately fine textured	Surface soils made up of clayey subsoil; the result of plan construction
	B. pH Characteristics	5.6 to 7.3 (typically slightly acid)	7.3 to 7.5 (control areas)
	C. Cation Exchange Capacity (meq/ 100g soil)	-	20.6 to 20.8 meq/100g (control area)
	D. Soil Organic Content (or TOC)	Typically high	TOC: 0.65% dry solids (control area)
	E. Water Retention Ability	a) available water capacity: 0.19 cm per cm of soil b) Permeability: to 2.0 cm per hour	May be somewhat different from published
II.	Ground & Surface Water Proximity		
	A. Surface Water	River ∿0.8 km to north; tributary ∿30 m to west	Same
	B. Ground Water	In upland wells, depth and quality variable (18 to 24 m to groundwater in river alluvium)	30 to 60 m to groundwater in this upland area
III.	Topographic Conditions		
	A. General Topography of Vicinity of Site	Rolling hills; 1 to 3% slopes.	-
	B. Topographic Relief of Area Visited	-	Field used in sampling program nearly level (result of alteration); rest of area more typical of vicinity.

(Continued)

IV.	Meteorological Conditions	
	A. Average Yearly Precipitation (cm)	84
	B. Distribution of Precipitation	70% in growing season
	C. Frost-free Period (days)	180 - 185
	D. Temperatures (Average daily maximum)	
	Summer (°C)	32
	Winter (°C)	≤0 (for five months)

*Includes information from Soil Conservation Service Personnel & Publications, USGS Surveys and/or State & University Surveys.

**Includes Arthur D. Little, Inc. observations and analyses from site visits, as well as interviews with facility personnel and representatives of waste generators and farms.

As indicated in Table 1, the soils of this agricultural region consist of silty clay loams which are deep and well drained; however, the specific area sampled contained a more clay-like soil due to past plant construction. The observation of high clay content in the sampled soils is corroborated by elevated values of cation exchange capacity (CEC) and a soil pH in the alkaline range. A major concern of the site operators is the possibility of modification of the agricultural soil due to the sodium content in the waste. Sodium, in high concentrations relative to calcium and magnesium cations, displaces these elements in the clay. Since hydrated sodium is larger than the displaced divalent cations, the clay structure becomes swollen and deflocculates, thereby restricting water movement through the soil.

A second concern of the site operators is long-term accumulation of heavy metals, with the potential for uptake by plants and salts at the soil surface. The high clay content, high CEC and alkaline pH of the soil favor attenuation of heavy metals. The low soil permeability retards migration of soluble salts through the soil profile.

Land Treatment Management

The land treatment site occupies 180 acres and had been in operation for two years prior to sampling. During the previous year the site had received 1.5 million gallons of sludge by subsurface injection, so as to reduce the potential for odors and runoff. The waste is transported in a Big Wheels® tank truck three to four times per day, seven days per week for ten months out of the year (waste applications cease in January and February). Storage capacity at the generating facility is limited to a 1900 gallon holding tank; during non-application periods, waste is discarded into trenches on site property. The land treatment site management has considered surface spreading (not sub-surface injection) the waste during the winter months since the cold weather reduces odors released by the sludge.

The Big Wheels® truck is used to apply the waste and is equipped with a three- knife subsurface application unit. Sludge is injected six to eight inches into the soil; depth decreases as the truck load lessens. The waste generator determines the rate of application according to the salt content of the sludge.

The soil and waste are mixed using normal agricultural procedures. Soils are amended by pH adjustments and nutrients as needed using labor and equipment provided by the farmers who lease the land. It is believed that due to waste application, 20-40 fewer pounds/acre of nitrogen have been applied to corn acreage and 40 fewer pounds/acre in fields growing milo.

At the site, the sludge is analyzed daily for total solids. Every two years, the soil is analyzed for pH, N, P, and K by the farmers. Occasionally organic matter and micronutrients are also monitored. Prior to sale, the waste generator reserves the right to analyze the crop for heavy metal content; if established limited are exceeded the waste generator is obligated to purchase the crop.

In addition to general monitoring activity, the waste generator has set aside a test plot, for which the sludge and soil are extensively analyzed. If soil salinity levels increase significantly, the waste generator will either apply gypsum to the soil (to decrease the sodium content of the waste relative to Ca and Mg) or replace the present crops with salt-tolerant ones.

Table 2 summarizes the responsibility for activity surrounding the land-treatment operation. Control over all aspects of the operation is in the hands of the waste generator. Company employees haul and apply the sludge with company-owned equipment on company-owned land. Outside involvement includes two local farmers who lease the land for commercial farming. However, the waste generator's supervisor meets twice a year with the two farmers to plan and coordinate disposal and farming activities in such a manner that sufficient acreage is available for waste disposal. Contact is maintained with the farmers at approximately two week intervals on an informal basis. Recordkeeping is excellent at the site.

TABLE 2. SITE MANAGEMENT AND RESPONSIBILITY

	Plans/Decides Manages/Supervises	Performs	Approves Checks
Storage	W.G.	W.G.	W.G.
Pretreatment	None		
Wastes Mixing	None		
Transport	W.G.	W.G.	F
Application		W.G.	
Soil Incorporation		F	
Solid Waste-Amendments	W.G./F	F	
Farming	W.G./F	F	W.G.
Monitoring	W.G./F	W.G./F	W.G.

W.G. = Waste Generator (same as site owner here)
F = Farmer

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

In sharp contrast to other land disposal options, land treatment can be managed so that the waste application area need not be irreversibly removed from any other potential practical usage. The basic reason is that plant-soil systems have a natural assimilative capacity for waste constitutents. If rates and total quantities of wastes applied are controlled so that the assimilation capacity of the site is not exceeded for any constituent of the waste, no potential future use of the site will be precluded. Assimilative capacity is both chemical specific and site specific. In other words, each chemical constituent of a given waste will be assimilated to a different extent at the same site; and the same chemical constituents will be assimilated differently at different sites.

The conclusions of the present study are limited to the evironmental acceptability of land treatment for secondary wastewater treatment sludge from one particular synthetics manufacturing plant, at one particular application site. The results cannot be generalized, either to wastewater treatment sludges from other manufacturing plants in the plastics and synthetics industry, or to other potential land treatment sites for the particular wastewater treatment sludge investigated. The field study findings do provide insight into the factors that should be considered in the design and operation of a land treatment site to ensure environmental acceptability. The field study results characterize, to the extent possible, actual practices at a land treatment site used for purposes of waste treatment rather than for purposes of research. Conditions of waste application were therefore given, and not under the control of the investigators.

CONCLUSIONS

The waste sludge as applied contained about 8.5% solids and 91.5% water. Approximately 2700 kg of waste solids/acre/year had been applied to the 180 acre site for two successive years prior to field sampling. The area had subsequently been planted in wheat, which was sampled just prior to harvest.

Analysis of the dried waste solids showed 18% metals, 23% TOC, 6% TKN, 22% sulfate, negligible chloride and 31% undertermined. Of the metals analyzed*, only chromium was found in significantly higher concentrations in the application area than in the control area. Based on the low measured concentration of chromium in the waste (54 μg/g of dried solids), the average measured level in the upper twelve inches of the application area (34 μg/g of dried soil) is considered anomalous.

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*As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V, Zn

Comparison of the mass spectra for extractable organic fractions of waste, application area and control area provided no indication of either biodegradation or persistence of organic components of the waste.

Grain samples from wheat grown in the application area showed no significant differences in metal content from similar samples obtained from the control area.

The applied waste had a high concentration of sodium (16% of the dried solids), relative to magnesium and calcium (0.2% and 0.07% of the dried solids respectively). This condition can lead to a deterioration of soil structure, particularly in the high clay content soils characteristic of the site. Excess sodium, relative to calcium and magnesium, promotes deflocculation and swelling of clay particles, thereby reducing hydraulic conductivity and assimilative capacity for water.

The waste generator (also the owner of the land) was aware of the problems associated with sodium-clay interactions and formulated the frequency and rate of waste applications to minimize the potential of salt build-up. Site personnel monitor the effects of salt upon the soil; gypsum and/or salt-tolerant plants will be used to mitigate these effects in the event that the sodium content is adversely affecting the soil and plant growth.

The high nitrogen content of the waste (almost 6% of the dried solids) and the high cellulose content act as beneficial soil amendments.

RECOMMENDATIONS

Because preliminary sampling results indicate incipient build-up of salts in the application area soils, monitoring of the site soils and plants should continue. This site provides an excellent opportunity to study land treatment at a site with a short, well-documented operating history.

SECTION 3

APPROACH

DATA COLLECTION AND ANALYSIS

Samples of the waste, baseline soil, and soil/waste mixtures were collected and analyzed for inorganic constituents and organic compound classes. Plants were collected and analysed to assess the extent of uptake of inorganic waste constituents.

The analytical protocol involved determining the following classical and inorganic waste parameters: pH, SO_4, and Cl^-, electrical conductivity (EC), cation exchange capacity (CEC), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V and Zn. Plasma emission spectroscopy and ion/chromatography were employed for inorganic species.

Analytical techniques employed for organic species included liquid chromatographic separation of organics into aliphatic, aromatic, and polar classes (LC-H, LC-A and LC-X, respectively), total chromatographic organics (TCO) and gravimetric (GRAV) analysis for volatile and non-volatile portions, and high resolution mass spectrometry (HRMS) for sorting classes by hydrogen saturation and heteroatom composition. The sampling and analytical methods are described in detail in the Appendix.

DATA INTERPRETATION

The analytical results from sampling the waste, the site receiving the waste, and a control site were compared to assess, insofar as possible, the relative decomposition, accumulation and migration of inorganic constituents and organic compound classes. The sampling and analytical program used in this study was designed to include sampling and analysis of appropriate control areas at the site so that any apparent concentration changes of waste components in application area samples could be differentiated from background levels. However, during preliminary site visits several factors were identified which would make it difficult to interpret any observed, apparent concentration changes. These factors include the following: an ideal control area was not available at the site; and, the chemical compositions of applied wastes were known to have varied over time.

The existence of many significant sources of uncertainty in the background data on the site made it desirable to provide some additional checks on the validity of the analytical data besides that provided by comparison of

TABLE 3. COMPARISON OF "TYPICAL" ELEMENTAL CONCENTRATION RANGES IN SOILS AND PLANTS WITH CORRESPONDING CONCENTRATION RANGES IN CONTROL AREAS USED IN THIS STUDY

Elemen	Typical Mean ppm Dry Soil (Range)[1]	Range ppm Dry Soil This Study[2]	Typical Range ppm Dry Plant Wt. Basis	Range ppm in Plant Ash This Study[5]
As	6 (0.1-40)	0.8-16	0.1-5[3]	1-16
B	10 (2-100)	2.1-9.2	5-30[3]	31-620
C	20,000	6,000-29,200	--	--
Ca	13,700 (7,000-50,000)	2,200-13,00	1,000-20,000	23,000-171,000
Cd	0.06 (0.01-0.7)	.3-.7	0.2-0.8[3]	1-4
Cr	100 (5-3,000)	7.9-65	0.2-1[3]	19-140
Cu	20 (2-100)	11-41	4-15[3]	69-290
K	14,000 (400-30,000)	2,300-8,400	20,400[4]	26,000-54,000
Mg	5,000 (600-6,000)	4,000-6,000	500-15,000[4]	14,000-40,000
Mo	2 (0.2-5)	1.7-3.3	0.2-5[3]	14-64
N	1,000 (200-2,500)	464-1,700	--	--
Na	6,300 (750-7,500)	22-440	--	940-10,000
Ni	40 (10-1,000)	9.6-31	10-10,000[4]	7-36
P	650	5,300-10,000	1,000-10,000[4]	17,000-168,000
Pb	10 (2-200)	24-280	0.1-10[3]	29-370
Se	7 (10-25)	0.1-0.5	0.1-2.0[3]	<.1-0.5
V	100 (20-500)	17-50	20-500[3]	3-90
Zn	50 (10-300)	41-110	10-300[3]	270-3,800

1. Bowen, H.G.M., Trace Elements in Biochemistry, Academic Press, Inc., NY, 1966.
2. CTL 0-6" Samples.
3. Alleway, W.H., Agronomic Controls Over the Environmental Cycling of Elements.
4. Berger, K.C., Sun Soil and Survival, University of Oklahoma Press, OK, 1976.
5. CTL Samples.

control and application area sample results. These checks are described below:

Inorganic Analysis

Validation of Control Samples --

The analytical data obtained in this study for control area samples from six landfarm sites are compared in Table 3 to typical concentration ranges found in soils and plants. Comparison of the soils data for the six sites indicates that almost all of the results obtained in this study are within typical concentration ranges. Exceptions are phosphorus (P), which was generally found in concentrations in excess of typical ranges, and sodium (Na) and selenium (Se), which were generally found in concentrations less than typical ranges. The selenium discrepancy may be due to volatilization of that element during the sample preparation procedure used in this study; the reasons for the sodium and phosphorus differences are not clear. Comparison of data on plants is of limited utility for several reasons, viz.: 1) plant uptake is species-specific; 2) uptake by a particular species is dependent on soil conditions; and 3) for the purpose of this study, elemental concentrations in plants have been expressed on an ash weight basis to compensate for the frequently poor physical condition of plants collected in the field. However, if we assume that the ash weight is usually on the order of 10% of the dry weight (the actual mean ash weight for all six control area samples in this study was 8.7% of dry weight), then the majority of results obtained in this study lie within typical ranges encountered in plants on a dry weight basis. In general, comparison of the results for control area samples in this study to typical elemental concentrations ranges in soils and plants suggests that there are no severe biases which would invalidate conclusions from the analytical data presented in this report.

Total Mass of Analyzed Parameters --

The sum of the masses of individual analyzed species in a sample of waste is a fraction of the total waste mass. For instance, if there were no species in the waste solids other than those determined in this study, the sum of all the individual masses should be approximately equal to 100%, depending on the uncertainty associated with the sampling and analytical methods. Inspection of the data presented shows that species determined in this study account for 68% of waste weight. The significance of this observation depends, of course, on the identity of the species that were not determined. Likely candidates are the elements Fe, H, O, Si and Al, all of which could be reasonably expected to occur in significant quantities in wastes of the type included in this study. In any case, consideration should be given to the presence of possibly substantial amounts of unidentified species in subsequent interpretations of the analytical data presented in this report.

Definition of Significant Pollutant Increases --

Interpretation requires some judgment about what constitutes a significant change in concentration of a given parameter relative to background levels. To this end, the results for total metals, Total Organic Carbon (TOC), and Total Kjelkahl Nitrogen (TKN), were expressed as ratios of total concentration in the application area to total concentration in the control area (APN/CTL).

Inspection of the data generated from six land treatment sites indicates that three elements - K, Mg, and P - show no significant increases above background, i.e., individual APN/CTL ratios for each of the elements at each site are close to 1.0 indicating that there is little difference in the actual concentrations of each of the elements between the APN and CTL area samples. The relative standard deviations of the mean APN/CTL ratios for these three elements are 33% (K), 9.1% (Mg), and 20% (P). Their mean relative standard deviation is approximately 20%; this number may provide a useful measure of the background variability of elemental concentrations in soils. Thus, for the purpose of this report, it has been assumed that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than $\pm$20% relative to the mean CTL area concentration (i.e., APN/CTL > 1.2).

The results for total metals, TOC and TKN in the wastes from all sites were used along with data obtained from the site owner on waste application rate (i.e., kg waste/acre/yr.) and waste percent solids, to estimate the number of years before one could expect to observe any increase of the elements analyzed in this study. The following assumptions were made:

1. Actual application rates have been the same as those given by the site operator;

2. All the waste generated for land treatment has been applied to the area which we sampled;

3. The waste has been incorporated uniformly into the top 12" of soil over the entire area described in #2; and

4. The waste composition has been constant and identical to that determined in this study.

The resulting estimates are discussed in more detail in chapter 4.

The steps in the procedure used to calculate the years of waste application necessary before one could expect to observe any increase above background were as follows.

Waste Application Rate --

The quantity kilograms of waste solids/acre/year was calculated from data supplied by the waste generator. For certain sites, the waste generator was able to provide an estimate of this quantity directly for other sites, where perhaps only an estimate of the annual volumetric waste generation rate was available, this calculation was performed according to the following equation:

$$\text{Kilograms of waste solids/acre/year} = \frac{\text{Annual volumetric mean generation} \times \text{Density of waste as applied} \times \text{\% solids in waste}}{\text{Acres of application area}}$$

In those cases where estimates of the waste density and % solids were not available from the waste generator, values obtained from laboratory analysis of waste samples collected during sampling visits to each site were used. As indicated in assumption 2 above, the value of the quantity "acres of application area" in the above equation was equal to the area in acres of the waste application area sampled in this study.

Annual Loading Rate of Individual Waste Species --
The quantity "kilograms of waste solids/acre/year" calculated in Step 1 was multiplied by the concentration in ppm of the element of interest determined in this study in waste samples collected from each site to give the annual loading of that element:

kg/acre/year x mg/kg (=ppm) of element of interest in waste solids = mg/acre/year

According to assumption 3, the waste was assumed to be incorporated uniformly into the top 12 inches of soil over the entire application area so the units of this quantity were assumed to be equal to mg/acre-foot/yr.

Annual Increase of Individual Waste Species --
The annual loading expressed as mg/acre/yr of each element of interest obtained in Step 2 was divided by an estimate of the average mass of one acre-foot of soil to give the predicted annual increase in concentration of each element of interest.*

Estimated Years of Waste Application --

The predicted annual increase in concentration of each element of interest was used to estimate the years of waste application necessary before one could expect to observe any increase above background of the elements analyzed in this study. The latter quantity depends on the detection limits of the sampling and analytical methods used for each element of interest. For example, the atomic absorption spectroscopic procedures used for analysis of many of the elements determined in this study involved digestion of ~1.5 g of soil and dilution of the resulting solution to 50 milliliters. Assuming that our instrumental method was capabile of detecting a change in concentration

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[The average mass of one acre-foot of soil was calculated as follows:

1 acre ~ 43,560 ft^3; 1 acre-foot =
43,560 ft^3 x 1 ft = 43,560 ft^3;
43,560 ft^3 x .0283 m^3/ft^3 = 1233 m^3;
average bulk density = 1.6 g/cm^3 = 1.6 x 10^3 kg/m^3 (cf. Overcash, M.R. and D. Pal, Design of Land Treatment Systems for Industrial Wastes Theory and Practice, Ann Arbor Science, 1979);
1233 m^3 (1.6 x 10^3 kg/m^3) 2 x 10^3 kg
Therefore,
(mg/acre-foot/yr) ~ 2 x 10^6 kg/acre-foot = $\frac{\text{mg of element of interest}}{\text{kg of soil-year}}$ =

ppm/year]

of the element of interest in that solution equal to 1 part per million, the corresponding concentration change of that element in the soil sample taken for analysis would be ∿ 30 parts per million:

$$\left(\frac{1\mu g}{mL} \times 50\ mL\right) / 1.5\ g \simeq 30\mu g/g = 30\ ppm\ in\ soil$$

The quantity ppm/year calculated in Step 3 was divided by 30 ppm to give the number of years of waste application necessary to observe a concentration change. Note that the "observable concentration changes" referred to here are not the same as "significant concentration increases" referred to in the preceding discussion.

For most elements determined in this study by atomic absorption (AA), the actual instrumental detection limit is probably lower than 1 ppm. However, since a systematic study of the detection limits of the combined sampling and analytical methods was beyond the scope of this study, the 1 ppm estimate may, in fact, be a more reliable estimate of the actual detection limits, given the uncertainty associated with the sampling methods.

Organic Data Interpretation

The principal objective of the organic chemical analysis program was to obtain data for a preliminary evaluation of the effectiveness of land treatment in degrading organic components of chemical wastes. To accomplish this objective it was necessary to characterize the organic components of the waste and to look for evidence of significant accumulation, degradation or migration of those components in the soil.

The organic analysis scheme provided for quantitative analysis of extractable volatile (TCO) and non-volatile (GRAV) organics, and of three polarity classes (LC-H, LC-A and LC-X) by liquid chromatography. Qualitative analysis of the organics by compound type was achieved by HRMS which provided data on heteroatom composition and the degree of compound saturation (R + DB values).

The combined qualitative and quantitative results provide insight into the extent of waste component degradation. For instance, an increase in polar species in APN area samples can be taken as an indication that the aromatic and aliphatic constituents originally in the waste have partially degraded since the byproducts of aerobic oxidation are generally polar oxygenated species. Typically, the organic analysis results do not permit determination of which waste components are being transformed into particular types of degradation products. However, the HRMS data do indicate which specific classes tend to persit in the soil column and which classes tend to appear as degradation products.

Accumulation of certain waste types can be determined by increases of aromatic and aliphatic classes relative to each other. For example, suppose the LC-H and LC-A fractions of extractable organics account for more than 50% of the organics in the APN 0-6 and 6-12 layers and in the control soil in

these fractions are only 10% of the total. The ratio of LC-A to LC-H in the waste is 0.24; in APN 0-6, 0.37 and in APN 6-12, 0.96. The absolute values of the LC-H and LC-A concentrations were lower in the APN 6-12 than in the 0-6. These types of trends are indicative of 1) preferentially degradation/or loss of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) in the APN soil compared to the CTL soil, without the appearance of oxidative degradation.

SECTION 4

RESULTS AND DISCUSSION

WASTE CHARACTERISTICS

Total Mass of Parameters

The percent of dried solids analyzed in the waste was 68.8% and is broken down as follows:

	%*
Metals	18.28
TOC	22.93
N	5.58
SO_4	22.00
Cl	0.0026
	68.8

*% of dried solids

Species not determined include Fe, H, O, Si, and Al. The high ratio of organic carbon to inorganic nitrogen can be observed from these data. This ratio was one of the reasons for land treatment of the waste.

Elemental and Inorganic Analysis

The results of analysis for total metals, TOC and TKN, in the waste for the site are presented in Table 4 below. From the data, one can observe the extremely high sodium concentration relative to the calcium and magnesium values. These data were used along with data on waste application rate (2.7×10^3 kg of waste solids/acre/year, as estimated by the site operator) to calculate an estimate of the years of waste application necessary before one could expect to observe any increase above background in the application area soil. Based on these results, observable increases in the application area at the time of sampling would be expected for Na, C, N (in decreasing order of predicted concentration). Although some of the assumptions used in this prediction may not be entirely valid, the calculation is believed useful as a reference point for considering the reasonableness of soil analysis results and helping interpret these results.

TABLE 4. INORGANIC WASTE ANALYSIS AND ESTIMATED YEARS FOR OBSERVABLE SOIL CONCENTRATION

Element	Waste Concentration (µg/g dried solids)	Estimated years of waste application for observable soil concentration change
As	4	*
B	24	*
TOC	22.93%	1
Ca	660	*
Cd	5	*
Cr	54	*
Cu	60	*
K	8,200	3
Mg	1,600	*
Mo	6.0	*
TKN	2.90%	1
Na	16.0%	1
Ni	44	*
P	6,100	4
Pb	50	*
Se	0.5	*
V	4.9	*
Zn	81	*

* = greater than 10 years

Organic Analysis

The waste itself was an aqueous slurry that was found to contain 33 mg/L of extractable organics. On the basis of the liquid chromatography (LC) separation of the extract, the organic materials were characterized as follows:

Aliphatic Hydrocarbons, volatile (TCO):	12% (4 mg/L)
non-volatile (GRAV):	46% (15 mg/L)
Aromatic Hydrocarbons, non-volatile (GRAV):	7% (.02 mg/L)
Polar Organics, non-colatile (GRAV):	35% (11 mg/L)

About 12% of the extractable organics will be lost as volatile aliphatic hydrocarbon. Non-volatile aliphatic hydrocarbons comprise the bulk of the LC organics. The High Resolution Mass Spectrometer (HRMS) analysis (Table 5) supports this finding in that 44.9% of the hydrocarbons contain less than four rings and double bonds (R + DB). The aromatic hydrocarbons (7% of the extractable organics) seem to be primarily made up of single ring structures such as benzene and toluene.

The ELCOMP assignments for these species show parent and fragment ions of 6-16 carbons, and molecular weights up to about 220.

The polar fraction of the waste is 35% of the LC fraction. The C, H, O, R + DB 0-4 species that account for 24% of the total matrix assignments are primarily fatty acid/ester mass spec (ms) fragments. ELCOMP shows that these include fragmentations with 1 to 4 oxygen atoms. The C, H, O, R + DB 4 category appears, based on ELCOMP, to also include some phenol fragment ions. There are also some indications of the presence of aliphatic sulfur compounds (C, H, S, R + DB = 0,1) and very low levels of C, H, N, O ms fragments.

SOIL CHARACTERISTICS

Wastes had been applied to the test plot soil for two successive years prior to sampling. Soil and plant samples were collected on July 13, 1978, which was 3 months after the second annual waste application.

Inorganic Analysis

Inorganic analytical data on soils is presented in Table 6. As previously discussed, for the purpose of this report, it was judged that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than $\pm$ 20% relative to the mean CTL area concentration (i.e., APN/CTL > 1.2 for the ratios of total concentration in application area to total concentration in control area). "APN/CTL ratios" are shown in Table 6 for total metals, Total Organic Carbon (TOC), and Total Kjeldahl Nitrogen (TKN).

Based on calculations, concentration increases were predicted for sodium, carbon and nitrogen (listed in decreasing order); increase was observed only for chromium, and not for any of the predicted elements. The APN/CTL ratio Cr was 2.2 (the Cd APN/CTL ratio is not considered significant due to the low concentrations involved). Cr would have had to be

TABLE 5. R+DB SUMMARY MATRIX FOR SITE WASTE SAMPLES*

R+DB	C,H	C,H,N	C,H,O	C,H,S	C,H,N,O	Total (from HRMS Analysis)
0				1.5		1.5
1	16.9		8.2	0.7	1.3	27.1
2	13.5		11.8	0.1		25.4
3	14.5	3.6	2.6	0.1		20.8
4	14.9		1.0			15.9
5	3.3		0.1			3.4
6	1.9	0.4	0.1			2.4
7	1.3	0.9			0.9	3.1
8	0.1					0.1
9	0.2					0.2

*All values in percent, normalized to 100%.

TABLE 6. INORGANIC ANALYSIS OF CONTROL AND APPLICATION SOILS

Element	Concentration in Soils (µg/g) dry wt.				
	CTL		APL		APN/CTL*
	0 - 6"	6 - 12"	0 - 6"	6 - 12"	
As	8	9	8	9	0.8
B	8.7	8.0	8.7	3.8	0.7
TOC	0.65%	NA	0.73%	NA	1.1
Ca	4,400	4,000	4,400	3,800	1.0
Cd	0.3	0.3	0.7	0.7	2.3†
Cr	20	11	26	41	2.2
Cu	20	18	21	19	1.1
K	8,400	4,700	1.0%	5,800	1.2
Mg	6,000	6,000	6,000	5,500	1.0
Mo	3.0	2.3	3.0	2.4	1.0
TKN	893	NA	977	NA	1.1
Na	440	370	500	340	1.0
Ni	31	27	30	28	1.0
P	1.0%	8,800	1.0%	9,000	1.0
Pb	31	29	32	29	1.0
Se	0.2	0.2	0.2	0.2	1.0
V	50	50	57	38	1.0
Zn	110	73	90	78	0.9

NA = Not Analyzed.

* = APN/CTL Ratio calculated as {APN (0-6) + APN (6-12)} / {CTL (0-6) + CTL (6-12)}.

† = Absolute levels of Cd are too small to attach significance to this ratio.

introduced into the application area at a concentration at least 200 times greater than that listed in Table 4 to account for the observed increase. Since none of the three elements -- Na, C and N -- for which observable increases were predicted showed any measured increases (even though they were present in the waste at levels considerably in excess of Cr), the reported Cr concentration may be anomalously high.

Data for pH, CEC, sulfate, chloride, and electrical conductivity are given in Table 7. The electrical conductivity and concentrations of SO_4 and Cl are slightly higher in the application area soil samples. The magnitude of increase in each of these parameters is too small to be related in a meaningful way to soil/waste interactive mechanisms, but the fact that there is an apparent increase may be an indication that salts are beginning to build up in the APN area.

Organic Analysis

Control Area Soils-Control samples were taken from 5 land treatment sites, consisting of composite 0-6" and composite 6-12". Soil cores from each site were analyzed to characterize the extractable organic materials that might be found in a range of natural soils. This characterization is important because of the difficulty in establishing control areas in terms of extractable organics. A "typical" control soil sample contains 150 mg/kg of extractable organic material, all in the GRAV range, that is polar (>80% in LC-X). The HRMS matrix analysis approach shows predominantly R + DB 1-4 hydrocarbons and oxygenates, with some R + DB 5-9 hydrocarbons and nitrogeneous materials. Little or no material in the R + DB 10 range was present.

This definition of a typical control sample constitutes one general fixed reference point for evaluation of data on application area soil samples. The other reference point is the waste applied to the land treatment site.

Table 8 presents data on the total organic carbon content and the quantity of extractable organic material in control soil samples. Figures 1-3 illustrate the results of the LC separation and HRMS analysis. It is obvious that a small and highly variable portion of the soil organic material is extracted by methylene chloride. Known types of nonextractable organics include high molecular weight polymeric materials, such as amino acids. Non-polar and moderately polar organic species of molecular weights up to 500 or 1000 are generally efficiently extracted from environmental samples by methylene chloride. All of the extracted material is in the GRAV range (b.p. >300°C) which is expected, since TCO range organics (b.p. 100 - 300°C) would be lost from soil by volatilization. Also expected is the observation that CTL 6"-12" samples have considerably lower levels of extractable organics than CTL 0"-6" samples.

Application Area Soils - The application area 0-6" depth (APN 0-6) and 6-12" depth (APN 6-12) samples were found to contain 93 mg/kg and 42 mg/kg, respectively, of extractable material. These quantities are not significantly different from the corresponding levels for the control samples: 135 mg/kg for CTL 0-6 and 8.7 mg/kg for CTL 6-12. Waste application to date, therefore, has not led to a significant accumulation rate or complete degradation of waste components.

TABLE 7. SITE SOILS: INORGANIC PARAMETERS

Sample	pH	C.E.C. me/100g	E.C. µmhos	$SO_4^=$ µg/g	Cl^- µg/g
Waste				22.0%	26
Soil:					
CTL 0-6	7.3	20.6	210	120	4
CTL 6-12	7.5	20.8	135	180	2
APN 0-6	7.1	22.8	370	120	7
APN 6-12	7.3	20.0	360	240	4

TABLE 8. QUANTITIES OF TOTAL AND EXTRACTABLE ORGANIC MATERIAL IN CONTROL SOIL SAMPLES

Sample	Organic Material, mg/kg	
	Total Organic Carbon	Extractable Organic
CTL 0-6"	6,500	135
CTL 6-12"	-	8.7

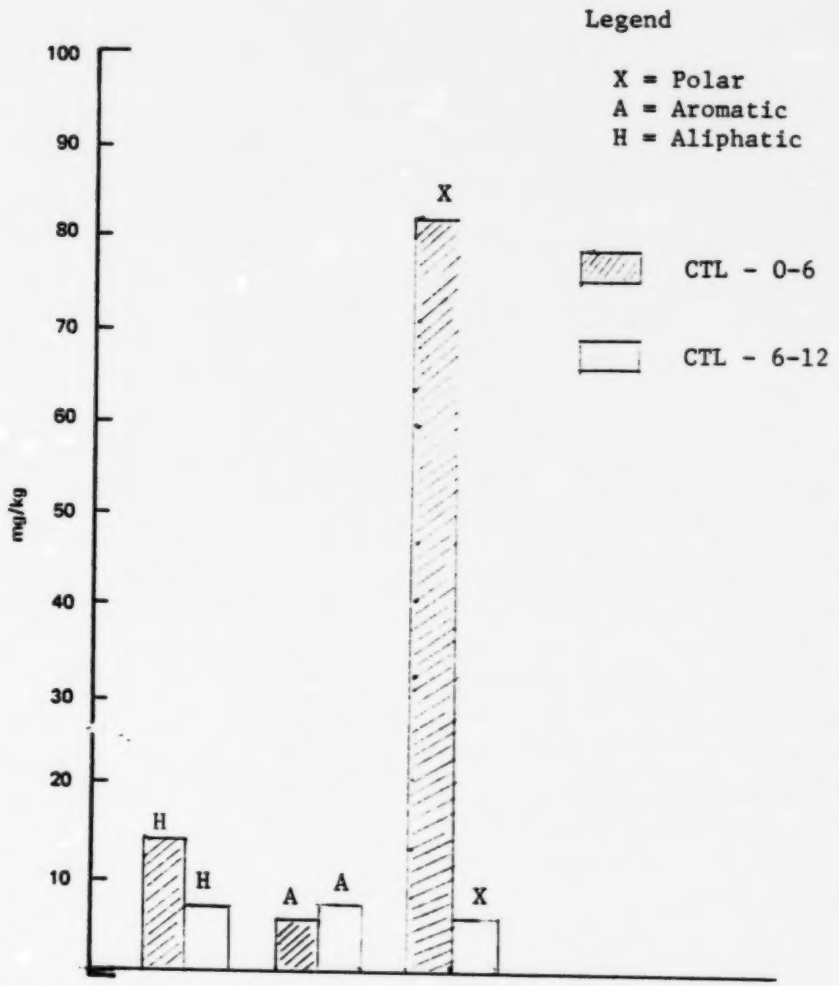

Figure 1. LC Results for CTL Samples

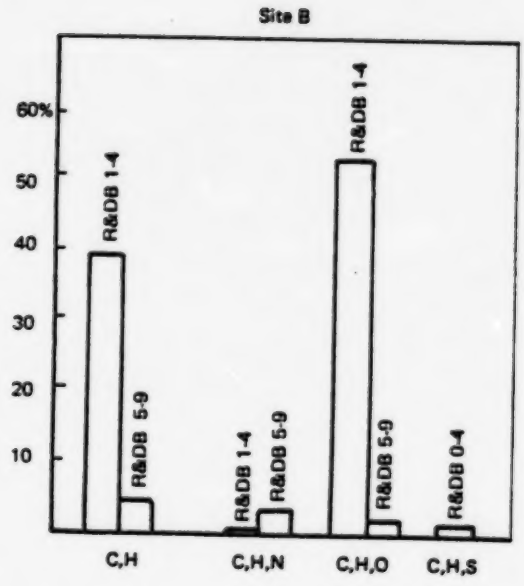

Figure 2. R + DB Clusters for CTL 0-6 Samples

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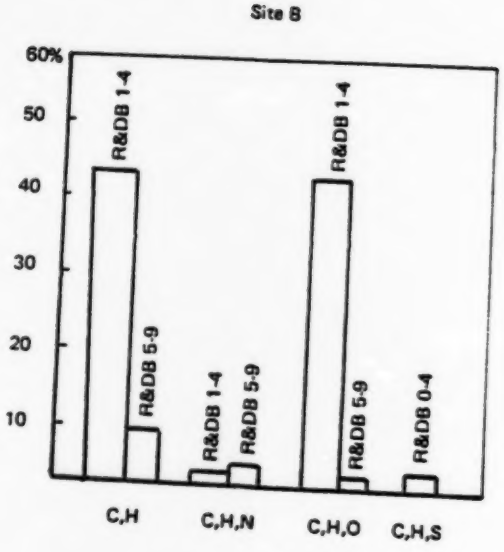

Figure 3. R + DB Clusters for CTL 6-12 Samples

Figure 4 presents the results of the LC separation of the site application area samples, as well as those of the corresponding waste and control area samples. Comparison of the APN 0-6 and waste sample extract results reveals that the APN 0-6 sample is relatively richer in polar organics (LC-X = 50% of total) than is the waste (LC-X = 35% of total). However, it is not clear whether this is related to degradation of the waste, since the CTL 0-6 sample contains more polar material than APN 0-6 on both a relative and an absolute basis.

The distribution of aliphatic and aromatic hydrocarbons in the APN 0-6 sample does suggest possible accumulation of waste components in the soil. Aliphatic (LC-H) and aromatic (LC-A) hydrocarbons account for 50% or more of the organics in both the APN 0-6 and APN 6-12 sample extracts, but 20% of the CTL 0-6 extract. (LC data for the CTL 6-12 extract are not reliable because of the very small total sample applied to the column.) There is no evidence for selective loss of the volatile (TCO) range aliphatic hydrocarbons (13% of waste vs. 10% of APN 0-6) from the application area.

The LC data provide some evidence of selective accumulation of aromatic vs. aliphatic hydrocarbons in the soil. The ratio of LC-A to LC-H are 0.12 in the waste, 0.62 in APN 0-6, and 1.2 in APN 6-12. For CTL 0-6, the corresponding value is 0.39.

In Figure 5, the R + DB cluster profiles, on a relative distribution basis, are plotted for the waste, APN 0-6, APN 6-12 and CTL 0-6 samples. Figure 6 presents similar profiles in which the R + DB values have been weighted to reflect the differences in quantities of extractable materials in the various samples. There appear to be no significant differences in the R + DB cluster profiles that can be interpreted in terms of the effectiveness of the land treatment process. Furthermore, within any given R + DB category there is a high degree of similarity in the elemental compositions of the ms fragments found in each of the five samples. No distinctive ions could be identified in either the waste or the application area samples that were not present in the CTL samples as well.

In summary, comparison of the application and control area samples data reveals no quantitative evidence for significant accumulation of waste components in the soil. Comparison of the waste and application area LC profiles provides some evidence suggestive of possible enrichment of the APN 0-6 sample in aliphatic and aromatic hydrocarbons, particularly in the latter. This conclusion must be regarded as tentative in the absence of supporting quantitative data on the overall rate of accumulation of waste organics in the soil.

PLANT ANALYSIS

The area examined at the site had been planted in wheat, with harvesting occurring just prior to the sampling date Plant samples from the application area were taller than those collected from the control area, possibly indicating increased fertility of the clay-like soils due to waste application.

Only grain was analyzed in this effort (see Table 9). Ratios between plant samples from application and control areas and between plant and soil samples in each area show no marked variations between the two areas sufficient to be indicative of enrichment of any element.

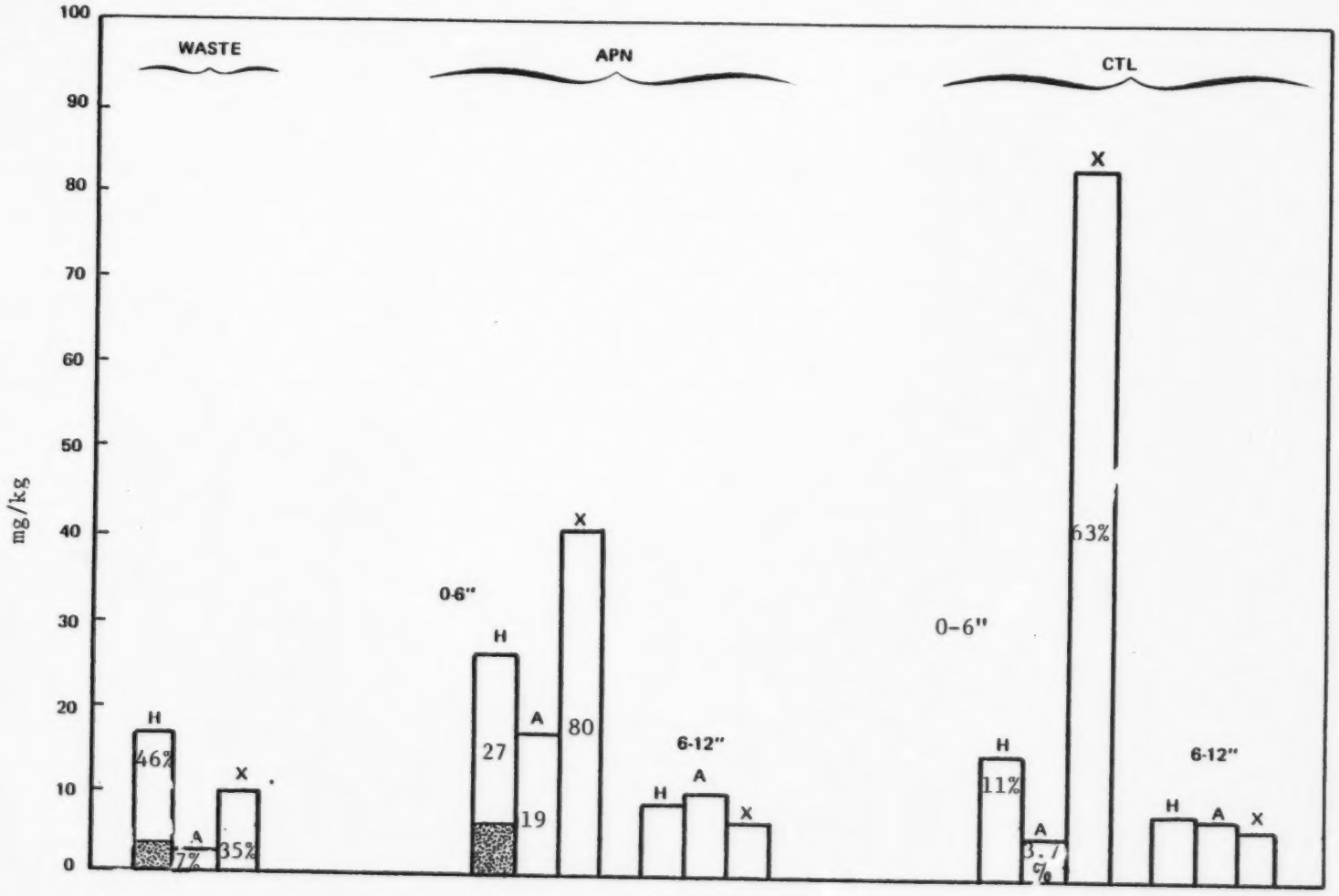

Figure 4. Histogram of LC Separation into Aliphatic (H), Aromatic (A) and Polar (X) Organic Classes

TCO fraction of extractable organics
GRAV fraction of extractable organics

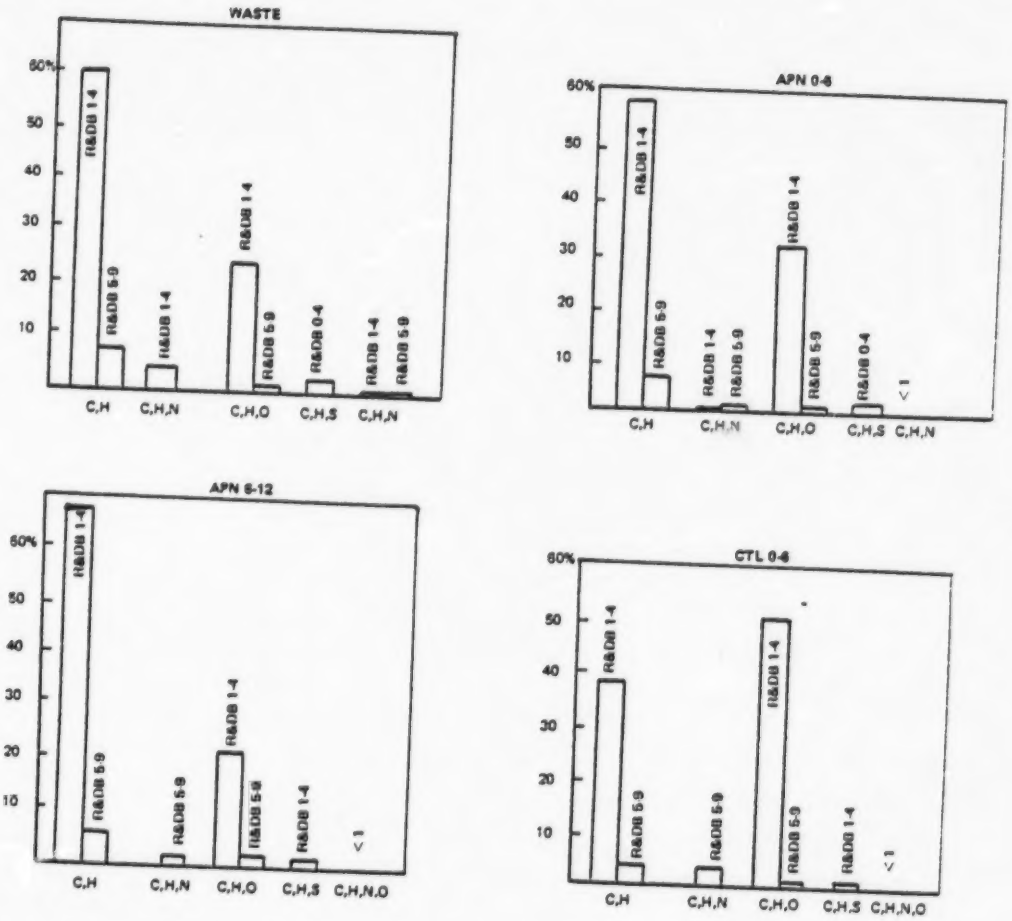

Figure 5. R + DB Cluster Profiles Relative Abundance Basis

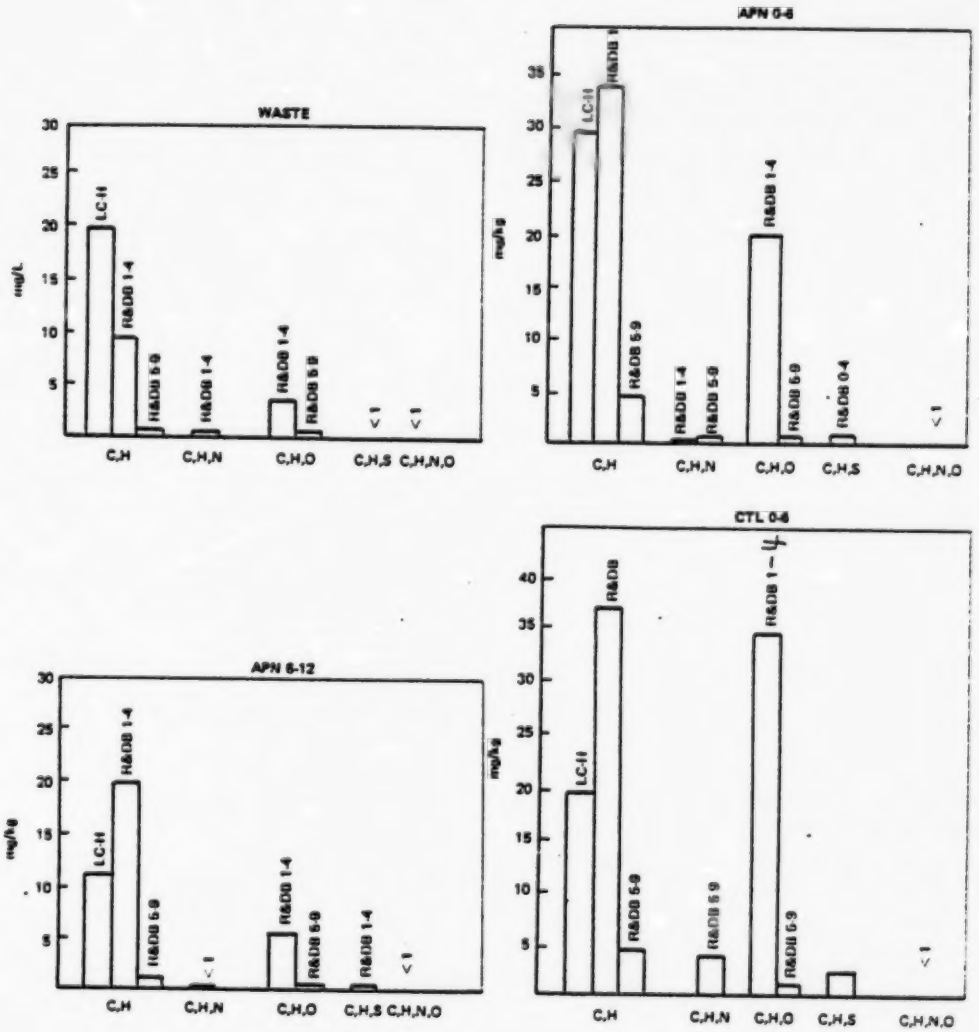

Figure 6. R + DB Cluster Profiles, Weighted Basis

TABLE 9. ANALYTIC RESULTS OF ASHED WHEAT SAMPLES

Element	Concentration in Ashed Wheat Samples (µg/g dried wt)		APN/CTL ratio		Plant Concentration (dried wt)/Soil Concentration (mean of depth)	
	CTL	APN	Wheat Grain	Soil	CTL	APN
As	5	1	0.2	0.8	0.59	0.13
B	36	39	1.1	0.7	4.3	6.24
Ca	2.3%	2.9%	1.3	1.0	5.5	7.1
Cd	6	7	1.2	2.3	20	10
Cr	19	21	1.1	2.2	1.2	0.63
Cu	230	210	0.9	1.1	12.1	10.5
K	6.2%	6.3%	1.0	1.2	9.5	8
Mg	3.5%	4.0%	1.1	1.0	5.8	7.0
Mo	17	14	0.8	1.0	6.4	5.2
Ng	2,700	3,500	1.3	1.0	6.7	8.3
Ni	19	33	1.7	1.0	0.7	1.1
P	16.8%	17.4%	1.0	1.0	17.8	18.3
Pb	29	26	0.9	1.0	0.97	0.85
Se	20.3	20.5	1.6	1.0	~1.5	~2.5
V	3	2	0.7	1.0	0.06	0.04
Zn	1,900	2,500	1.3	0.9	20.8	29.8
% Ash	2.5	2.3				

Results from this sampling effort indicate that present loading rates and number of applications to date have not resulted in observable differences between plants grown in control and application area. Plant parts can contain elements at higher levels than seeds. Because levels of metals in soils in the application and control areas are so similar, it is not expected that plant parts other than grain would contain unusually high levels of metals. This hypothesis is further reinforced for this location by the neutral soil and high CEC which would tend to provide good attenuation of most metal species.

APPENDIX

METHODS OF SAMPLING AND ANALYSIS

DATA COLLECTION PROCEDURES

Several approaches were used to collect data from the six field sites selected for study. Information sources included published surveys such as those produced by the Soil Conservation Service and/or local universities and state agencies. Where feasible, information gathered from interviews with site or industry personnel along with site observations were utilized to confirm or adjust such information for location specificity.

FIELD SAMPLING

The field sampling and analysis program was designed to provide information on the following:

1. The rate and extent of waste degradation,
2. The migration of inorganic species,
3. The accumulation of waste constituents in the soil, and
4. Bioaccumulation of inorganic species in vegetation.

To this end, measurements were made of the concentration of various chemical species in soil and vegetation samples taken from waste application and control areas. The species selected for analysis were those that occur as a direct result of the land cultivation operation and/or transport of any constituents of the wastes.

Sampling Methods

Sampling Locations--

At each site, samples were taken from (1) the area where waste had been applied and (2) the best identifiable control area. The ideal control area would have been upwind and upgradient of the waste application area, but in all other respects would have been identical to that area except that no waste had been applied. Selection of an appropriate control area was a problem at the majority of sites for a variety of reasons. In general, the design and operation of most sites did not include provision for a bona fide control area as described above. More specifically, problems included substantial variations in soil characteristics, drainage patterns and vegetation occurring within small distances; and uncertainty about the history of waste application outside the boundaries of the present application site. In all cases, a "control" area

was selected which necessitated the least compromise in the requirements stated above. In both control and application areas, samples were collected from a 4 x 4 grid covering the area. Wastes were collected from storage facilities or other sources, selected so as to assure that the samples were representative of the waste that was actually applied.

Sample Types--

The types and numbers of samples collected at each site included at a minimum the following:

	Control Area	Application Area
1) Waste	1 Sample	
2) Soil	2 Samples	2 Samples
3) Soil-Waste Mixture	-	2 Samples
4) Vegetation	1 Sample	1 Sample

Core samples of soil and soil-waste mixture were taken with a sampling tube. The resulting cores were 1" in diameter and 12" in length. These samples were divided in the field into two subsamples corresponding to 0-6" soil depth and 6-12" soil depth. Bulk samples were subsequently coned, quartered, and riffled to obtain amounts of sample appropriate for each analysis. Vegetation samples were collected from the same control and application areas from which soil samples were obtained. Unless noted otherwise, composite vegetation samples were prepared from whole plants minus roots. There were no opportunities for sampling surface water, runoff, or groundwater at any site during the sampling visits made.

CHEMICAL ANALYSIS

Inorganic

Analyses of inorganic parameters were conducted on the waste samples, soil and soil-waste mixture composite samples from application and control areas, and vegetation composite samples from application and control areas. Analytical methods used for determination of inorganic parameters are shown below. DTPA-Extractable metals are those metals which may be available for biological uptake.

Parameter	Method
B, Cu, Cd, Cr, Cu, K	HNO_3-$HClO_4$ digestion, plasma emission spectroscopy
Mg, Mo, Na, Ni, P, Pb, V, Zn	
As, Se	Hydride evolution, atomic absorption spectroscopy

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Total Organic Carbon (TOC)	Combustion, gravimetric
Total Kjeldahl Nitrogen (TKN)	Digestion, distillation, volumetric
Sulfate	0.1 M LiCl extraction, ion chromatography
Chloride	H_2O extraction, volumetric $Hg(NO_3)_2$ titration
Cation Exchange Capacity (CEC)	Volumetric
Electrical Conductivity (EC)	Conductivity Meter
pH	pH Meter
DIPA-extractable metals	DTPA extraction, plasma emission spectroscopy

Organic

The organic analysis scheme is shown schematically in Figure 7. The methodology involved:

1. Solvent extraction with methylene chloride;
2. Quantitative analysis of volatile and non-volatile organics;
3. Liquid chromatographic separation of the extracts to divide the organics into three polarity classes: aliphatic hydrocarbons, aromatic hydrocarbons, and polar species; and
4. Qualitative analysis of organic compound classes present by high resolution mass spectrometry.

Each of the steps of the methodology is described in further detail below.

Extraction--

The method adopted for isolation of organic components from the waste and soil samples was extraction with methylene chloride. Methylene chloride is a solvent which gives high extraction efficiency for a wide range of organic compound types. In particular, it is generally effective for non-polar and moderately polar, hydrophobic organics, which are the types of compounds that dominate many current lists of compounds of concern. It should be recognized, however, that polymeric, humic, proteinaceous materials, very polar, water-soluble, or soil-bound species will not be efficiently extracted. It should also be noted that these non-extractable species, if isolated, would generally not be amenable to available analysis techniques. An organic compound which is extractable from a waste sample may not be extractable from a corresponding soil sample because of soil bonding. Since non-extractable organics are probably less likely to be transported into plant cells, they may be of less environmental concern.

Control and application area soil samples (ca 100 g) were Soxhlet extracted with methylene chloride (ca 200 mL) for 24 hours. Waste samples were

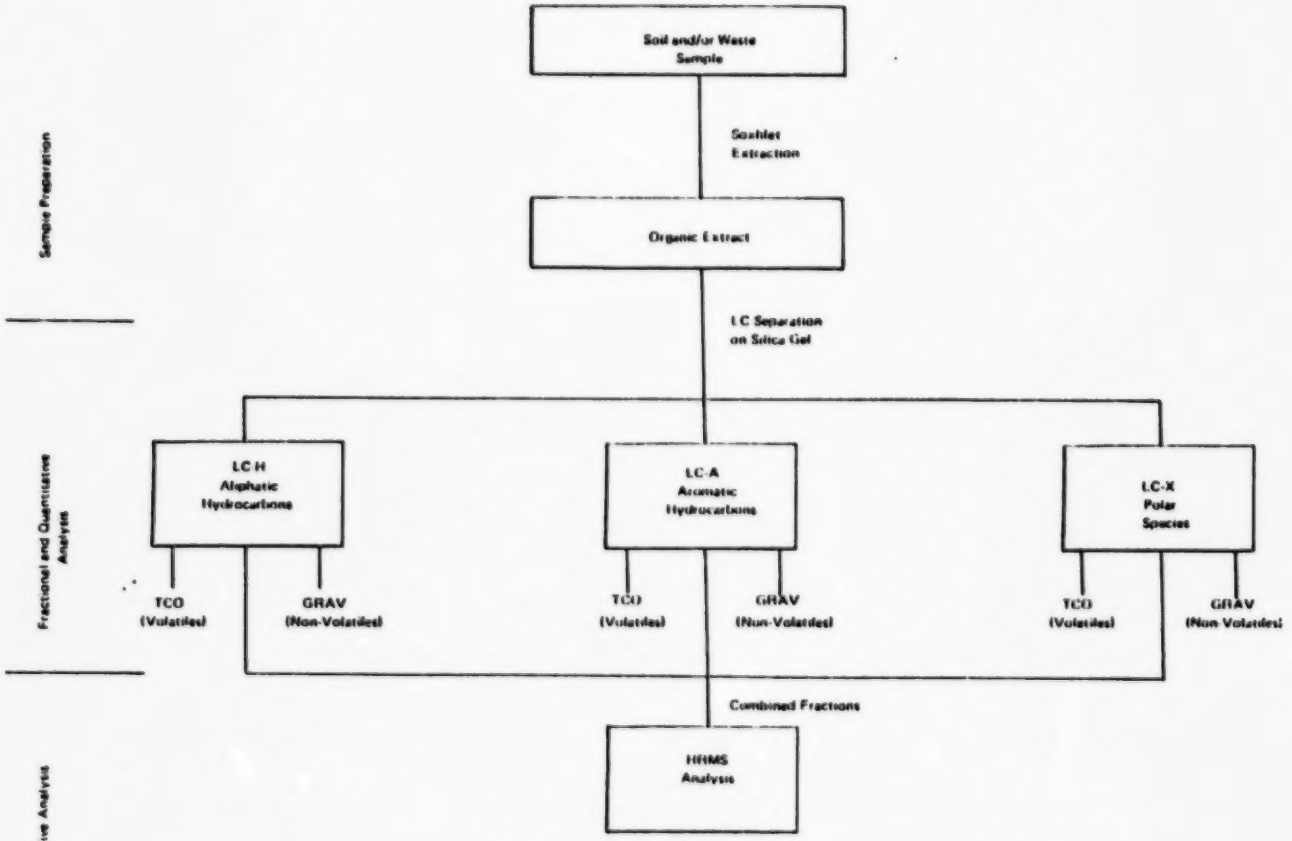

FIGURE 7. FLOW CHART OF PROPOSED ORGANIC ANALYSIS SCHEME

subjected to Soxhlet extraction, or to liquid-liquid separatory funnel extraction (3 times 100 mL of solvent per liter of waste), depending on their physical state. The methylene chloride extracts were concentrated to 10 mL final volume by use of Kuderna-Danish evaporative concentrators.

Quantitative Analysis--

Total Chromatographable Organics (TCO)--The Total Chromatographable Organics (TCO) analysis is a gas chromatographic (GC) analysis procedure that uses a flame ionization detector. A 1-5μL aliquot of the sample is injected. Resolution of individual QC peaks is not intended. The total integrated detector response is used to derive a single estimate (mg) of the quantity of material in the 100-300°C boiling point range.* The detection limit for a complex sample mixture is on the order of 50 ppm (w/v) in the solution injected. This corresponds to 0.5 mg total in the 10 mL sample extract.

Gravimetric Analysis (GRAV)--The GRAV procedure is a quantitative analysis of non-volatile components (materials above 300° boiling point range) of the sample extract. An aliquot of the organic solution is evaporated to constant weight, over silica gel, in a tared weighing dish. The practical detection limit is on the order of 0.1 mg in the 1 mL sample taken for GRAV analysis. This corresponds to 1 mg total in the 10 mL sample extract.

Liquid Chromatographic Separation--

A liquid chromatographic (LC) separation on silica gel was used to separate the extracted organics according to polarity. This is a lowresolution technique that has been demonstrated at Arthur D. Little, Inc. to provide reliable separation of organic components into three classes as indicated below.

LC-H: Aliphatic Hydrocarbons

LC-A: Aromatic Hydrocarbons

LC-X: Polar Organics (oxygenates, amines, etc.)

Details of preparation of the silica gel LC column have been published. The methylene chloride extracts were applied to the column after solvent exchange into cyclohexane. The elution sequence used in this program was as follows:

LC-H: 15 mL of pentane

LC-A: 15 mL each, sequentially, of 20% methylene chloride in pentane; 50% methylene chloride in pentane; and methylene chloride

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* Arthur D. Little, Inc., studies using model compounds have shown that n-hexadecane (b.p. 303 C) defines a reasonable break point between TCO and GRAV range materials.

LC-X: 5 mL each, sequentially, of 5% methanol in methylene chloride; 20% methanol in methylene chloride, and 50% methanol in methylene chloride.

Each fraction was analyzed by TCO and TRAV procedures as described above. The fractions were then recombined prior to HRMS analysis.

The LC procedure was originally scaled for 15-100 mg samples applied on column. However, the total amount of material available for some samples in this program was 10 mg. Quantitative recovery from the column was 70-100% when samples containing about 10 mg or more were used, but 50% for very small samples.

The reproducibility of the extraction and LC separation for these samples was checked by running duplicate LC columns on a site application area soil extract. The results are shown in Table 10.

High Resolution Mass Spectrometry--

High resolution mass spectra were obtained on the recombined LC fractions for each of the landfarm sample extracts. A Dupont (CEC) 21-110 B high resolution mass spectrometer, using a glass inlet and solids probe for sample introduction, was employed. Spectra were recorded on photoplates. The basic spectral data were then obtained by a photoplate reader and the position and intensity of the lines transferred directly to a laboratory data system (LDS). This is the HIRES output. The LDS, based on a Data General Elipse S/200 computer, was used for subsequent HRMS data processing.

The high resolution mass spectrometer is capable of measuring masses of ions in the spectrum with an accuracy of better than 0.001 atomic mass unit. Data from the HRMS analysis are reported to four decimal places in m/e (mass-to-charge ratio). The high accuracy and precision makes it possible to take advantage of the mass defect characteristics of atoms and use their exact masses to compute elemental composition assignments for the observed ions. The theoretical mass can be calculated for all "plausible" combinations of elements corresponding to a given mass. "Plausible" combinations are defined by the analyst, based on a preliminary manual examination of the HIRES data. The objective is to allow all of the elemental compositions (C + H; C + H + S; C + H + Cl, etc.) that are necessary to characterize the range of the sample chemistry, but to minimize the computation time and the number of incorrect, "near-miss" match assignments. The theoretical and measured masses are next compared and a "match" is identified when they agree to within a specified value, typically 0.002 or 0.003 atomic mass units. This information constitutes the ELCOMP output.

The ELCOMP output listing normally includes 400 to 1000 lines detected in the spectrum, their intensities, and 500 to 2000 associated chemical composition data. The approach used for interpreting this large quantity of data was to sort the assigned elemental composition into classes according to heteroatom composition (i.e., C,H; C,H,O; C,H,N; C,H,S) and degree of hydrogen unsaturation indicated by rings and double bonds. The R + DB value provides a convenient means of organizing data into probable chemical compound categories. Some examples will illustrate this point:

TABLE 10. REPLICATE EXTRACTIONS AND LC SEPARATIONS ON A SITE SOIL SAMPLE

	% Water	Dry Wt. Extracted (kg)	Extract TCO (mg)	Extract GRAV (mg)	Extract Total (mg)	Total (mg/kg)
Before LC Fractionation						
Sample 1: APN 0-6	15.9	0.0966	ND	9.0	9.0	93.2
Sample 2: APN 0-6	15.6	0.1090	ND	8.0	8.0	73.4
After LC Fractionation						
Sample 1: APN 0-6						
LC-H			0.82	1.67	2.49	25.8
LC-A			0.39	1.17	1.56	16.1
LC-X			ND	4.00	4.00	41.4
						83.3
Sample 2: APN 0-6						
LC-H			ND	1.17	1.17	10.7
LC-A			1.30	0.50	1.70	15.6
LC-X			ND	5.30	5.30	48.6
						74.9

for an n-paraffin, C_6H_{14}, R + DB = 0

for phenol, C_6H_6O, R + DB = 4

for benzothiophene, C_6H_6S, R + DB = 6

for anthracene, $C_{14}H_{10}$, R + DB = 10

for benzopyrene, $C_{20}H_{12}$, R + DB = 15

All paraffins or other saturated species such as acyclic alcohols and sulfides will always be in R + DB group 0. A species must have an R + DB value of 4 or more to be aromatic, and R + DB value of 7 or more to be a naphthalene, an R + DB value of 8 or more to be a polychlorinated biphenyl (PCB), and so on. The R + DB values were grouped in this report as follows: R + DB = 0, 1 R + DB 4; 5 R + DB 9; 10 R + DB 14; and 15 R + DB.

Similar calculations can be made for any species of interest. This approach does not differentiate among the different isomers of any compound class, such as anthracene and phenanthrene, in R + DB 10.

The R + DB and elemental composition values were then used to sort all of the data from HRMS analysis into a compact matrix first according to the R + DB value and second according to the elemental composition of each of the ions identified. This approach presents a simple view of the overall composition of a sample from a highly complex spectrum. This approach requires that all ions finally included in the matrix are parent (molecular) ions. However, a large number of fragment ions in the spectra complicates the analysis. In interpreting the HRMS data it is also necessary to account for isotope ions (e.g., ^{13}C and ^{37}Cl), and composition assignments with large experimental errors. Consequently, in developing the R + DB matrix, certain restrictions were applied in an attempt to eliminate interferences and questionable calculated compositions. The restrictions applied were:

Molecular Weight: Ions below 90 atomix mass units were excluded to minimize the interference from fragment ions.

Error: Calculated compositions which differed from measured values by more than 2 millimass units were excluded.

Isotopes: All calculated compositions that included isotopes such as ^{13}C, ^{34}S, and ^{37}Cl were excluded.

R + DB: Only compositions with integral R + DB values were included, thus excluding fractional R + DB values which arise from fragment ions.

Carbon No.: A minimum carbon number limit was set for each R + DB class.

For this report, the individual intensities of all ions within each R + DB and element group were summed to give a single estimate of the abundance of that group. For each composite sample, these estimates were subsequently displayed in a condensed form as shown in Figure 8.

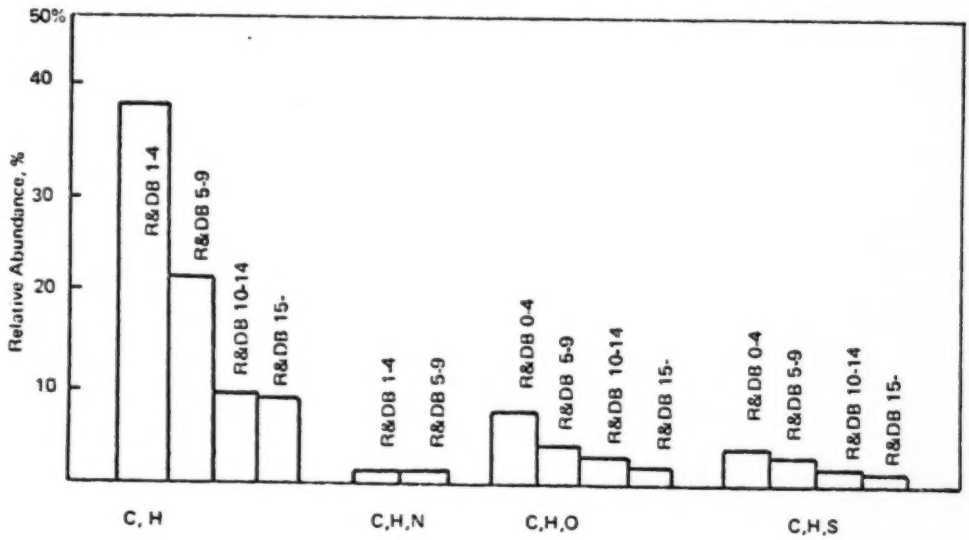

FIGURE 8. EXAMPLE OF DISPLAY OF R&DB AND ELEMENTAL COMPOSITION GROUPINGS FOR A SOIL SAMPLE EXTRACT